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# Investigating the Electronic Structure of Fluorite Oxides: Comparison of EELS and First Principles Calculations

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**Abstract.** Energy loss spectra from a variety of cubic oxides are compared with *ab-initio* calculations based on the density functional plane wave method (CASTEP). In order to obtain agreement between experimental and theoretical spectra, unique material specific considerations were taken into account. The spectra were calculated using various approximations to describe core-hole effects and electronic correlations. All the calculations are based on the local spin density approximation to show qualitative agreement with the sensitive oxygen K-edge spectra in ceria, zirconia, and urania. Comparison of experimental and theoretical results let us characterize the main electronic interactions responsible for both the electronic structure and the resulting EEL spectra of the compounds in question.

### Introduction

In the past few years, there have been growing efforts to apply modern first-principles materials modelling tools as a framework for accelerated materials design and development. One area where such modelling efforts can make unique contributions is in the understanding of the evolution of the mechanical properties of advanced nuclear fuels (key to many future reactor designs). Establishing a damage evolution model for oxide fuels currently however suffers from inaccurate models, partly due to a lack of experimental validation. As damage mechanisms need to be extrapolated for the expected 50 year lifetimes of reactors, the absence of models that accurately address the energetic contributions

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of all the induced defects limits the applicability of theoretical models. Direct validation of the purposed theoretical techniques, in their application to oxides, requires direct experimental measurements of structure, composition and electronic interactions at the nanometer scale – in particular to observe the atomic and electronic structure of relevant point defects and their extended complexes. This can be resolved by acquiring images and electron energy loss spectra (EELS) using a scanning transmission electron microscope (STEM). Since we are interested in oxide fuels, the oxygen *K*-edge is chosen to compare experiment and theory directly, and here we attempt a first validation of the theory by studying three fluorite structured oxides - ceria, zirconia, and urania.

We employ the local spin density approximation (LSDA+U) with unique materials considerations using the CASTEP code. The materials considerations include correlated f-states, magnetic ordering, and in view of the direct comparison to STEM/EELS the core-hole effect.

## Methods

### *1.1. Experimental Analysis*

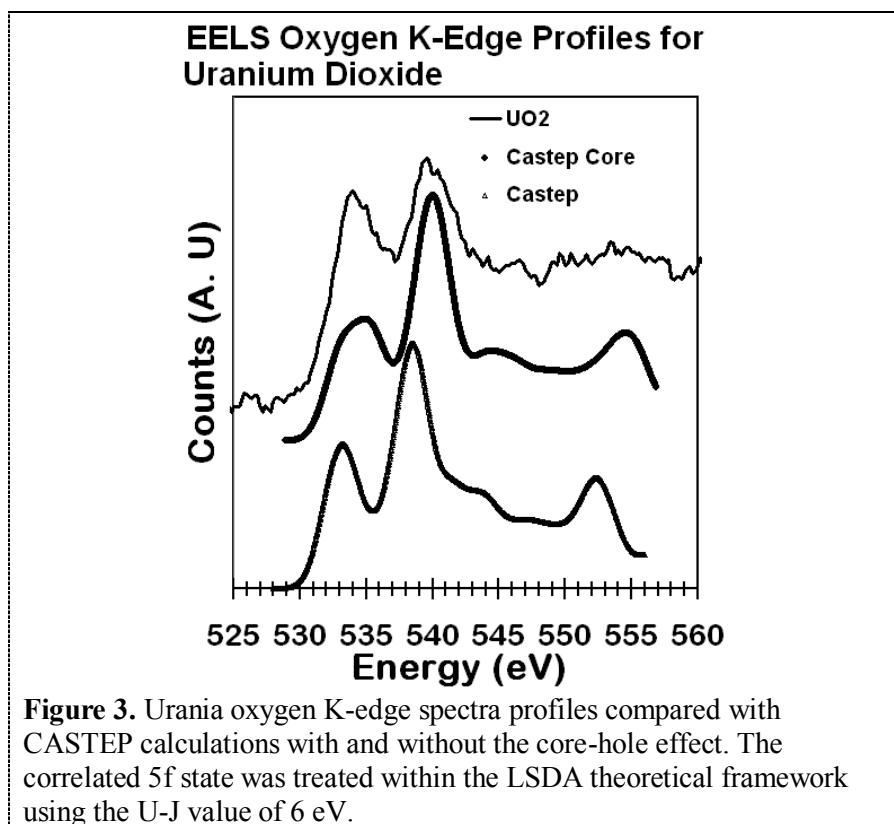
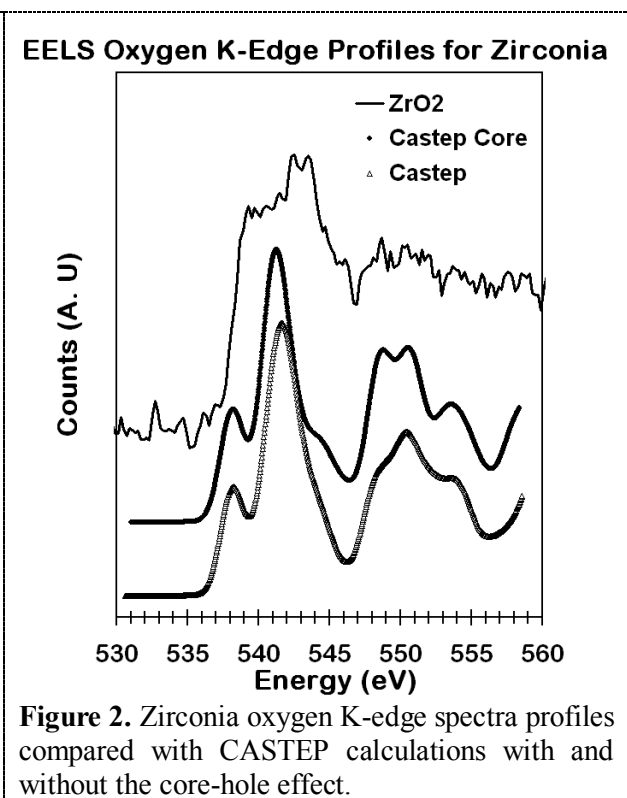
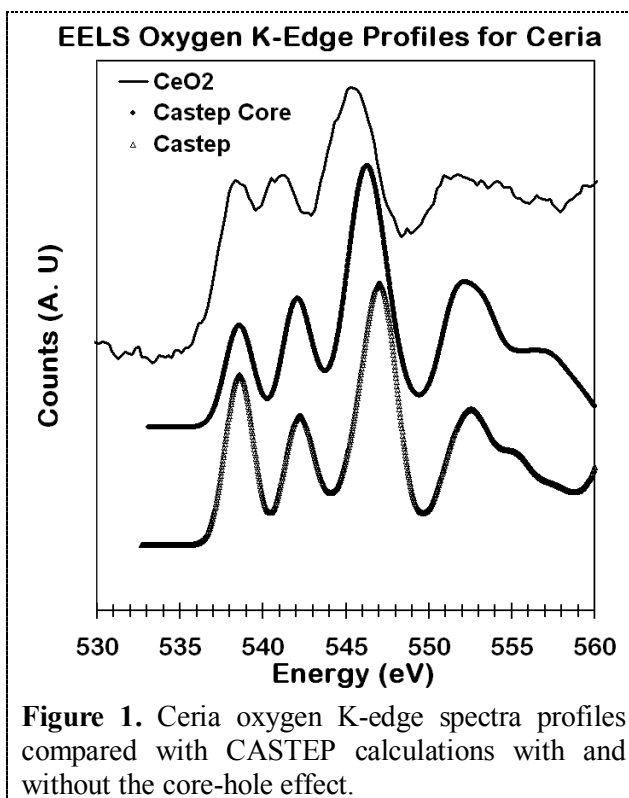
Standard ceria, zirconia, and urania powder samples were dispersed on 3 mm standard holey carbon TEM grids. The experimental spectra were obtained from the double corrected FEI Titan at Lawrence Livermore National Laboratory (LLNL) operating in STEM mode at 300 keV. EELS spectra were obtained with a Gatan Tridiem electron energy loss image filter. The energy resolution is 0.7 eV based on the full-width half maximum of the zero-loss peak. The acquisition time for each spectrum is 5 seconds with 0.1 eV/pixel dispersion.

### *1.2. Theoretical Treatment*

All calculations presented below are carried out using the CASTEP code [1,2]. CASTEP uses a plane wave basis set and pseudopotentials within the density functional theory formalism. Perdew Burke Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used to describe exchange–correlation functional. To describe localized f-orbitals of U we employed the LSDA+U approach [3] with an effective Hubbard *U* value of 6 eV. Ultrasoft pseudopotentials were generated on the fly, and one core electron was removed from a relevant core level when performing core–hole calculations [4]. All core–hole calculations were carried out using supercells sufficiently large to eliminate unphysical interactions between periodic images. Previous experience from all-electron calculations gives 8–10 Å as a recommended distance between images. Crystal symmetry is reduced when a core hole is introduced in a supercell. All calculations were carried out by using reduced symmetry rather than by ignoring point group symmetry altogether; even a reduced symmetry allows calculation speed to be increased by considering only *k*-points in the irreducible part of the Brillouin zone.

## Results

Normalized electron energy loss oxygen *K*-edge spectra in ceria, zirconia, and uranium dioxide are compared below with the theoretically predicted spectra from the CASTEP codes. All normalized spectra were aligned based on the concavity change in the first peak.



## Discussion

In the cubic fluorites, the oxygen K-edge is sensitive to local the binding environment. Using the appropriate atomic structure and material considerations one can now model the electronic structure of these oxide materials. The comparison of the oxygen K-edge EELS spectra across the various oxides validate qualitatively that the latest CASTEP results for these materials is valid.

In the cubic fluorites we show agreement with and without the core-hole effect taken into account.

Using the local spin density approximation with unique materials considerations using the CASTEP code we show qualitative agreement across the fluorite oxides. In the three cases we have considered for ceria, zirconia, and urania. The materials considerations include correlated f-states, magnetic ordering, and in view of the direct comparison to STEM/EELS the core-hole effect.

## Conclusion

The oxygen K-edge EELS spectra for the oxides agree qualitatively with the theoretical electronic structure calculations based on the CASTEP code. Taking into account the core hole effect shows even greater qualitative agreement with experimental EELS spectra. Further work will render the atomic spectra with the inclusion of defects and vacancies to compare with future experimental results.

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